

Report as of FY2007 for 2007ND150B: "Effective Delivery of Iron Nanoparticles by Amphiphilic Polysiloxane Graft Copolymeric Vehicles for Groundwater Remediation"

Publications

- Other Publications:
 - ◆ Krajangpan, S. , Jarabek, L., Jepperson, J., Chisholm, B., Bezbaruah, A. September 7 2007. Protecting Iron Nanoparticles from Oxidation by Non-target Compounds and Their Effective Subsurface Delivery Using Amphiphilic Polysiloxane Graft Copolymers, ND/SD ESPCoR 6th Biennial Joint Conference 2007, Fargo, ND. [Poster]
- Conference Proceedings:
 - ◆ Krajangpan, S. , Chisholm, B., Bezbaruah, A., December 11 2007. Comparative Studies of Colloidal Stability of Bare and Amphiphilic Polysiloxane Graft Copolymer Coated Iron Nanoparticles and Their TCE Degradation Kinetics. ISNEPP 2007 Nanotechnology in Environmental Protection and Pollution, Ft. Lauderdale, FL. [Presentation]
 - ◆ Krajangpan, S., Elorza, J., Bezbaruah, A., Khan, E., Chisholm, B., December 11 2007. Nitrate Removal by Zero-Valent Iron Nanoparticles Entrapped in Calcium Alginate. ISNEPP 2007 Nanotechnology in Environmental Protection and Pollution, Ft. Lauderdale, FL. [Presentation]

Report Follows

Effective Delivery of Iron Nanoparticles by Amphiphilic Polysiloxane Graft Copolymeric Vehicles for Groundwater Remediation

Introduction/ Background on Research Topic

An increasing number of laboratory and field studies illustrate the potential of metal particles for degrading organic and inorganic species susceptible to reduction reactions [1-8]. Nanoparticles are attractive for remediation of various contaminants because of their unique physiochemical properties [9, 10]. Various chlorinated aliphatic hydrocarbons [11] and toxic metals [12, 13] can be remediated using metal nanoparticles such as zero-valent iron nanoparticles (nZVI). Metal particles/nanoparticles have also been used for the remediation of groundwater contaminated with chemicals used in explosives [14-19] and arsenic [19-22].

The effectiveness nZVI for groundwater remediation depends upon the effective delivery of the nanoparticles to the water/contaminate interface without flocculation and severe oxidation. To accomplish effective delivery of nZVI, a delivery system that provides for dispersability and colloidal stability of individual nanoparticles in water is required. In addition, the delivery system should protect the nZVI from severe oxidation by dissolved oxygen and water and provide an affinity for the water/contaminate interface.

Colloidal stability of nZVI has been accomplished using surfactants [23]. The hydrophobic “tails” of the surfactants physically absorb onto the nZVI surface while the hydrophilic “heads” inhibit flocculation and allow for suspension in the aqueous medium. While surfactants provide colloidal stability in water, the highly reversible nature of surfactant absorption limits its application as a delivery system for ground water decontamination since desorption will be favored when the nanoparticles are transported through surfactant-free ground water. In contrast, high molecular weight, amphiphilic polymers show essentially irreversible absorption and, thus, are more suitable as a delivery system for ground water remediation [24, 25].

Saleh *et al.* [26] have shown that amphiphilic triblock copolymers with an A-B-C triblock microstructure are effective delivery systems for nZVI. The triblock copolymers were produced using atom transfer radical polymerization (ATRP) in conjunction with a post-polymerization ester-hydrolysis step and a post-polymerization sulfonation step. The results of the research demonstrated enhanced colloidal stability and an increased affinity for a water/organic interface provided by the amphiphilic triblock copolymer. The amphiphilic triblock copolymers synthesized and evaluated by Saleh *et al.* [26] showed promising results with respect to enhanced colloidal stability of nZVI and the creation of a thermodynamic affinity of the nanoparticles for the water/contaminant interface. However, kinetic studies showed a decrease in the rate of contaminant degradation by the polymer-modified nZVI as compared to unmodified nZVI [27]. The reduction in contaminant degradation rate was attributed to low permeability of the contaminant through the film absorbed onto the nZVI. In addition to issues associated with contaminant degradation rate, the synthesis method required to produce the triblock copolymer structure is quite sensitive to impurities and oxygen and quite slow. Further, catalyst residues can be difficult to remove. Despite 15 years of intense research, ATRP is not being practiced commercially to any great extent. As a result, there exists a need to prepare tailored, multifunctional polymeric materials using a cost-effective, commercially-viable synthetic route that could serve as a highly effective delivery system for nZVI.

Considering the requirements of an effective delivery system for nZVI, functionalized amphiphilic polysiloxanes are an ideal class of polymers for the application. **Figure 1** provides a schematic representation of amphiphilic polysiloxane graft copolymers (APGCs) that could be easily synthesized and evaluated.

The hydrophobicity of the polysiloxane polymer backbone will protect the nZVI from excessive oxidation by creating a barrier to water while also creating an affinity of the coated nZVI for the water/contaminant interface as illustrated schematically in **Figure 2**. Since polysiloxanes have a very low glass transition temperature (-120°C) and are highly soluble in most hydrocarbons, they will readily allow permeation of organic contaminants such as arsenic to the nZVI surface providing fast, efficient contaminant remediation. Additionally, the versatility of the hydrosilylation reaction enables tailoring of the polysiloxane polymer backbone chemical structure to enhance contaminant specificity.

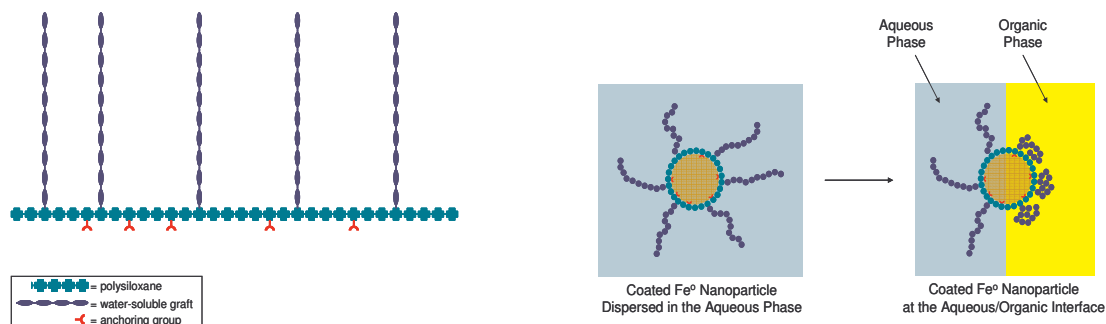


Figure 1. A schematic representation of amphiphilic polysiloxane graft copolymers (APGC) **Figure 2.** A schematic representation of the polymer coated nanoparticles in water and at the water/contaminant interface.

In addition to possessing the ideal characteristics for nZVI delivery system, this class of polymers can be easily synthesized from a wide variety of commercially available starting materials. For example, Gelest® Inc. sells a variety of poly(dimethylsiloxane-co-methylhydrosiloxanes) copolymers with varying methylhydrosiloxane content and molecular weights as well as poly(methylhydrosiloxane) homopolymers of varying molecular weight. With regard to precursors for the generation of hydrophilic polymer grafts, Clariant® sells an array of monovinyl-terminated PEGs of varying molecular weight. Thus, with this class of graft copolymers, extensive structure-property relationships can be developed by varying polysiloxane backbone molecular weight, hydrophilic polymer graft content and molecular weight, and anchoring group content.

Description of the Critical State or Regional Water Problem to be Investigated

Arsenic compounds are often found in contaminated groundwater [28]. A trivalent arsenic [As(III)] contamination is a major concern in southeast North Dakota (568 sq mile area in Sargent, Ransom and Richland counties are affected) [29]. The contaminated area is primarily comprised of farmland and a few small cites including Hankingson, Lindrud, Wyndmere, and Milnor. Sampling done since 1979 in that area indicated arsenic concentration as high as 1.5 mg/L. Remedial investigation completed by North Dakota Department of Health between 1982 and 1986 indicated widespread occurrence of elevated groundwater arsenic concentration. The elevated concentration of arsenic was attributed to, in part, to the use of arsenic-laced grasshopper bait used in the 1930s and 1940s to control grasshopper population. Arsenic trioxide, sodium arsenate, Paris Green, and other arsenic compounds were mixed with bait material (e.g. oats) and applied to farm field.

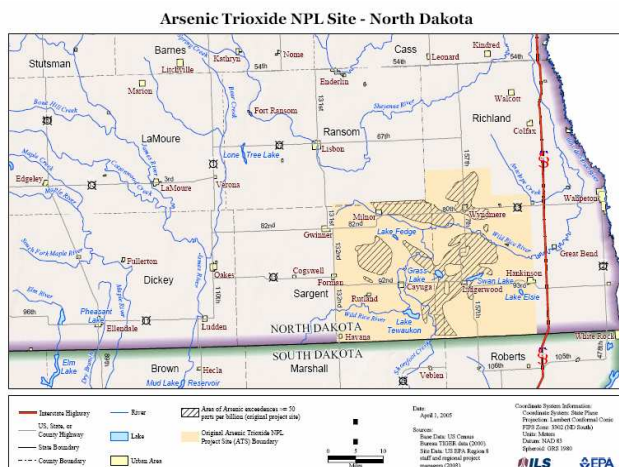


Figure 3. Arsenic Contaminated Area in SE North Dakota [29]

In addition, there are concerns about the TCE in North Dakota and Minnesota, especially, at the Baytown Ground Water Contamination Site in Washington County, Minnesota. They have looked at nZVI as a potential remedy for source zone and at-well applications [30]. RDX is a common nitramine explosive and one of the major groundwater contaminants in military facilities. RDX, explosive, when ingested, is known to cause tremors and convulsions leading to death. Though presently not reported in alarming level at the Air Force Base at Minot (ND) it may also be major of the concerns in the future.

Research Progress

The progress is summarized below:

Task I: Synthesis and characterization of APGCs

Carboxylic acid-functional APGCs containing polyethylene glycol grafts (PDMS/PEG/AA) were successfully synthesized. The APGCs were synthesized by hydrosilylation using PtO_2 as a catalyst. The proton absorption peaks at δ 0.4-0.5 ppm and δ 1.4-1.6 ppm in the ^1H NMR spectrum (**Figure 4a**) correspond to methylene protons created as a result of successful hydrosilylation of the vinyl functional precursors to the hydride functional polysiloxane copolymer.

The carbon absorption ^{13}C NMR spectrum (**Figure 4b**), has verified that the hydrosilylation reaction has occurred. The Carbonyl peak has a quartet at δ 158.0-158.9 ppm. Poly(ethyleneglycol) peaks appear between δ 59 ppm and 78 ppm. The tert-butyl carbonyl and its methylene carbon are located at δ 150.6 ppm, and δ 29.0 ppm, respectively. The same procedure was used to produce APGC varying the relative molar concentration of carboxylic acid groups to PEG grafts. With the varied ratios, all five formulations of PDMS/PEG/AA, A (70/25/5), B (62/36/2), C (72.5/21/6.8), D (67/29/4), and E (65/32/3), were successfully synthesized and characterized.

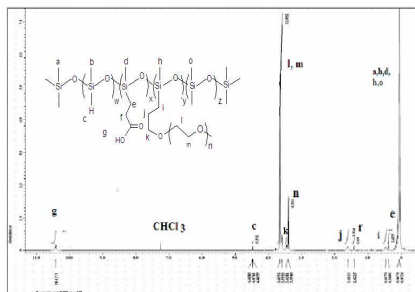


Figure 4a. A proton NMR spectrum of APGC.

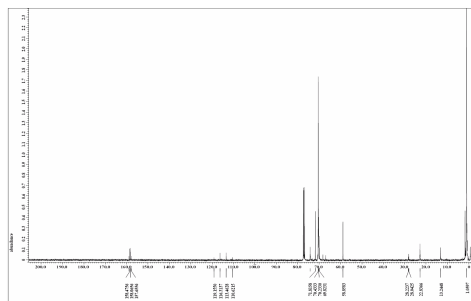


Figure 4b. A carbon NMR spectrum of APGC.

Task II: Synthesis and characterization of nZVI

Iron nanoparticles (nZVI) were successfully synthesized as per method laid out in my 2007 award proposal. The synthesized nZVI has average particle size of 35 nm. The particles sizes were analyzed by transmission electron microscope (TEM) over 300 particles (**Figure 5a, 5b**). BET specific surface was determined to be 25m²/g. SEM/EDS data indicate that iron is the most abundant mineral (84.34%), with, a smaller amount of oxygen (15.66%, in the oxide shell) on the nZVI (**Figure 6**). The shell prevents particles from spontaneously igniting in the atmosphere, yet allows contaminant access to nZVI in solution [31].

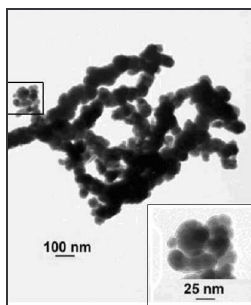


Figure 5a. TEM image of nZVI synthesized by the researcher's group.

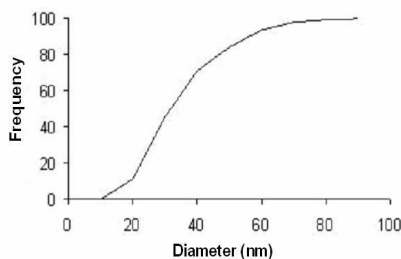


Figure 5b. Size distribution curve for synthesized nZVI

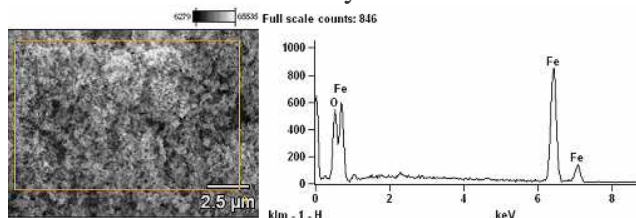


Figure 6. SEM/EDX image of fresh nZVI synthesized in the laboratory. The EDX result indicates 84.34 %iron and 15.66 %oxygen on nZVI.

Task III: Polymer coating of nZVI and sedimentation rate measurements

Aqueous slurry of nZVI was combined with 5, 10, and 15 g/L APGC polymer solutions of all five formulations. The mixture was sonicated for 30 min followed by gentle end-over-end rotation for 72 h to disperse the nanoparticles and allow the polymer to absorb on the surface of the nanoparticles. The APGC coated nZVI were then filtered and washed multiple times to remove any excess non-adsorbed APGC.

The colloidal stability of the APGC coated nZVI was then evaluated by measuring sedimentation rates of nanoparticle suspensions using a UV-spectrometer (at a wavelength of 508 nm). The sedimentation studies were done with five replications for each batch. **Figure 7** displays representative data illustrating the effect of APGC composition on colloidal stability of nZVI. From the figure, it can be seen that modification of the APGC coated nZVI have decreased

sedimentation rate and the magnitude of the decrease was a function of APGC composition. The APGC with the highest concentration of carboxylic acid anchoring groups provided the highest colloidal stability. These results confirm that the proposed approach for enhancing nZVI colloidal stability is valid as is the synthetic process for creating novel carboxylic acid-functionalized APGC.

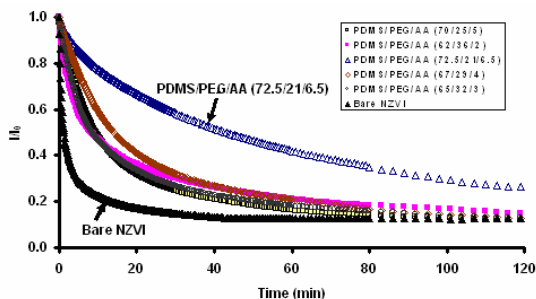


Figure 7. Sedimentation studies of APGC coated nZVI (PEG = polyethylene glycol and AA = acrylic acid). Ratio represents weight percent of each component. Marked decrease in sedimentation rate was observed for APGC modified nZVI as compared to bare nZVI.

Task IV: Degree of oxidation by non-target compound

The degree of oxidation was determined by quantitative SEM-EDX peak area. The EDX peak area analysis provides an approximate surface corrosion by percent Fe:O elemental composition. The analyses show 84.34:15.66, 49.71:50.29, and 68.03:31.97 for fresh nZVI, bare nZVI and APGC coated nZVI, respectively (**Figure 6, 8, 9**). The results indicate using APGC coated nZVI had significantly decreased nZVI surface corrosion. However, excess oxidation might have occurred during the washing process. Therefore, sample preparation needs to be modified and this study needs to be repeated.

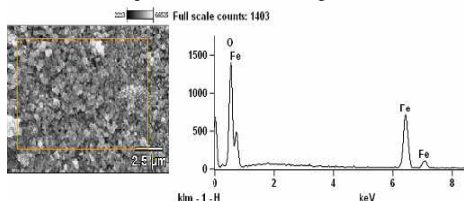


Figure 8 SEM/EDX image of bare nZVI in aqueous solution. The EDX result indicates 49.71 %iron and 50.29 %oxygen in the nZVI.

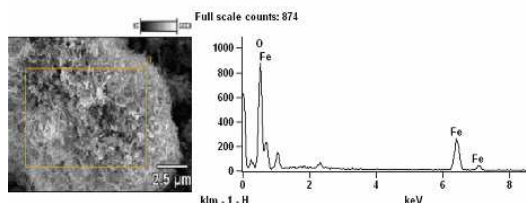


Figure 9 SEM/EDX image of APGC coated nZVI in aqueous solution. The EDX result indicates 68.03 %iron and 31.97 %oxygen in the nZVI.